

Modeling Hydrogen Generation from Hydroreactive Chemical Hydrides

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Abstract

Experimental and modeling results are presented that characterize the hydrogen (H₂) generation process when a lithium hydride (LiH) or lithium aluminum hydride (LiAlH₄) solid shape or powder is fully immersed in water. The reaction itself is fast, but what truly controls the rate of H₂ generation is the mass transfer of reactants and products to and from the hydride solid-water interface. Primary accomplishments of this study were demonstration of how variables such as surface area, temperature, pressure, product solubility, and water quality affect the rate of H₂ generation, and, with the help of experimental data, development of a mathematical model, based on mass and energy balances for a reacting system.

Keywords

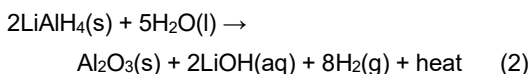
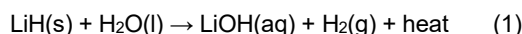
Hydrogen generation reactions; Dense hydrogen storage; Lithium hydrides; Reaction modeling.

Introduction

Hydroreactive materials, including LiH and LiAlH₄, offer a hydrogen-dense and fast-reacting method of generating a high-purity pressurized hydrogen (H₂) supply when contacted with water. They have particular application for fueling a polymer electrolyte membrane (PEM) fuel cell [1] in remote locations by drawing on a local water source. The hydride materials under study are stable, lightweight, and transportable in a backpack. Additionally, their reaction products are easily removed from a batch-type vessel, allowing for quick refueling.

Reaction Mechanism and Chemistry

The two hydrides of interest for this study react exothermically with water as follows to generate H₂:



The reaction itself is very fast, however, the actual rate of H₂ generation is governed by the mass transfer of reactants and products to and from the hydride solid surface, for example, the movement of hydroxides/oxides and H₂ away from the reacting surface, against the incoming flow of fresh water.

The reaction process is depicted in Figure 1. The concept shows bulk solid hydride and water phases, with a reaction

and mass transfer zone in between. Near the interface, fresh water reactant must migrate through a counter current flow of H₂ gas plus hydroxide as it dissolves into the bulk water phase. It is this exchange of materials that governs the rate of reaction, including the net rate of H₂ generation, and consumption of hydride.

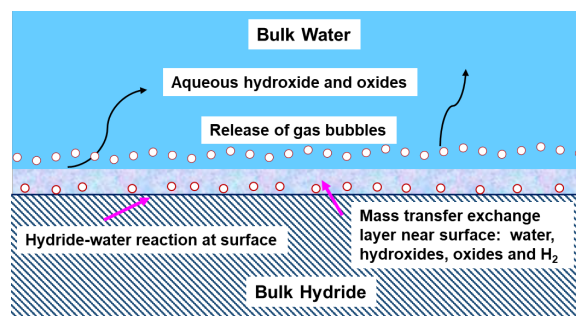


Figure 1. Hydride-Water Reaction Mechanism.

As is typical with this type of multiphase surface reaction with mass transfer, a number of variables including surface area, temperature, pressure, reaction kinetics, and water quality control the H₂ generation rate.

For many fueling applications, it is desired to generate H₂ either at a defined rate, or as rapidly as possible. And usually high purity and conversion efficiency are essential. Thus it is important to understand, and account for how all the variables mentioned above affect the desired production and quality of H₂.

Experimental

This investigation focused on the H₂-generating reaction of solid LiH and LiAlH₄ pellets and powder while fully immersed in water. An experimental system was designed and built (Figure 2) for collection of data over a range of variables. The variables studied in this particular report include:

- Hydride material in the form of both solid cylindrical pellets and 100 μm powder.
- Initial water temperature.
- Water volume.
- Fresh vs. salt water (seawater).
- Vessel pressure (maintained constant during experiments).
- Reaction rate of single vs. multiple pellets.

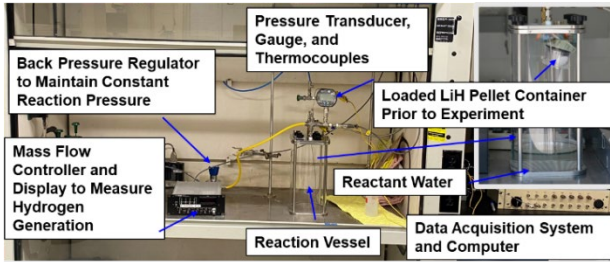


Figure 2. Experimental System for Collecting Hydride Hydrogen Generation Data.

The LiH was obtained from Albemarle Corporation in the form of 97%, < 100 μm powder. Solid pellets were pressed from the powder into 25 mm x 5 mm discs at near fusion density. Each pellet contained nominally 1.74 g LiH, capable of producing 0.44 g or 5.35 standard liters of H_2 .

The LiAlH_4 was sourced from Sigma-Aldrich as 95%, 10 mm x 6 mm pellets, weighing approximately 0.5 g and theoretically producing 0.11 g or 1.39 standard liters of H_2 .

Experiments were typically conducted batch-wise in a large excess of water (800 ml). The hydride sample was initially held above the water, while the vessel interior headspace was maintained at a defined pressure with a pure H_2 atmosphere. To start the reaction process, the weighted hydride container was released into the water, where it quickly sank to the bottom. As the hydride began reacting, H_2 bubbled through the water and into headspace, exiting the vessel and passing through the back pressure regulator and the mass flow meter. The back pressure regulator maintained a near constant system pressure throughout the duration of the reaction. Recorded data included hydrogen flow rate, vessel pressure, bulk water temperature, and temperature inside the hydride container. Experiments were typically designed to investigate one particular variable, while holding other variables constant.

Mathematical Model Development

A primary goal of this work was to develop a reaction model as a means of predicting H_2 generation according to the variables mentioned above. Some general data and knowledge about the reaction process were known, but additional data from experimental testing were needed to create a useful model.

The mathematical model for predicting hydrogen generation was developed from fundamental equations that characterize conservation of mass and energy for a reacting system. In all equations, the subscripts 'w' and 'p' denote a property of water or the hydride pellet respectively, while infinity (∞) represents a location in the bulk surroundings sufficiently far from the reaction to be unaffected by any change. Initial values, represented with a '0' subscript are taken at 20 $^\circ\text{C}$.

The time varying mass balance for a reacting system shown by equation 3, relates the effective volume of water interacting with the system, V_w , surrounding the surface reaction that takes place as water reaches the pellet.

$$V_w \frac{dC}{dt} = k_0 e^{\frac{-E_a}{R}(\frac{1}{T} - \frac{1}{T_\infty})} A_p (C_{sat} - C) \quad (3)$$

$C(t)$ represents the concentration of the product lithium hydroxide (M), k_0 is the initial mass transfer coefficient (m/s), E_a is the activation energy (J/mol) of the reaction, R is the ideal gas constant (8.314 J mol $^{-1}$ K $^{-1}$), $T(t)$ is the temperature at the reaction site (K), and $A_p(t)$ is the surface area available for reaction.

The corresponding energy balance, equation 4, gains terms from the heat of reaction, ΔH , and heat transfer around the reaction through a lumped heat transfer coefficient, h , that accounts for conduction and induced convection. C_p and ρ_p are the specific heat capacity (J kg $^{-1}$ K $^{-1}$) and density (kg m $^{-3}$) of the hydride pellet.

$$\rho_p C_p V_p \frac{dT}{dt} = -\Delta H k_0 e^{\frac{-E_a}{R}(\frac{1}{T} - \frac{1}{T_\infty})} A_p (C_{sat} - C) - h A_p (T - T_\infty) \quad (4)$$

For these equations, the rate of reaction is modeled by the Arrhenius equation ($k = A e^{\frac{-E_a}{RT}}$) with rate constant units of length per time. The equation for $\Delta H(t)$ is taken from a correlation of electrolytic solutions as used by Leckey, et al. [2].

$$\Delta H = 4.18 (-4900 + 18.8 (C/\rho_w)^{0.5} (T - 298)) \quad (5)$$

Additional parameters arise from the time-dependence of C_{sat} and h . Due to the expected nature of an initial ramp up in C_{sat} and convection, both functions are approximated in the form shown by equation 6.

$$X = X_0 \text{Tanh}\left(\frac{t}{t_x}\right) \quad (6)$$

Time parameters t_{eq} and t_0 are used respectively to capture the ramp up of C_{sat} and h some time into the reaction.

Concentration of the metal-hydroxide product is taken to be at saturation level at the surface due to the fast nature of the reaction in comparison to the time scale of diffusion. In order to account for reduction in pellet size as the extent of reaction rises, the simplifying assumption was made that all parts of the hydride pellet react equally so pellet surface area, A_p , is able to be directly related to the pellet geometry through an additional conservation of mass equation.

With all other physical properties defined, the remaining six unknown variables needed to solve concentration and temperature profiles for a reaction of given chemical hydride size and dimensions are: V_w , the initial mass transfer coefficient (k_0), the activation energy (E_a), the maximum heat transfer coefficient (h_0), and the time parameters t_{eq} and t_0 .

Results and Discussion

Effect of Initial Bath Temperature

Figure 3 shows the H₂ generation of single LiH pellets in fresh water over the temperature range of 16.7–40.0 °C, as system pressure is held constant at 221 kPa.

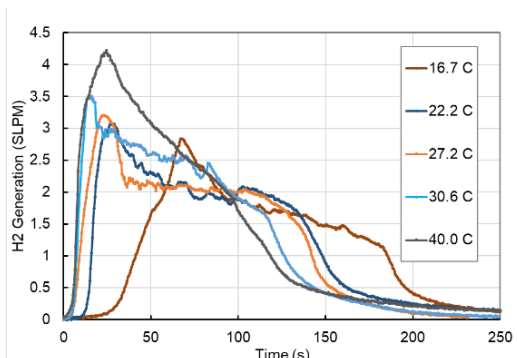


Figure 3. H₂ Generation for a Single Pellet at Various Initial Bath Temperatures.

As predicted by the Arrhenius equation, the rate constant – and thus H₂ generation rate – are strong functions of temperature. Peak rates generally increase with temperature while the time for complete reaction decreases. Integration of the generation data shows >95% conversion for all temperatures. Typically the heat of reaction increased the bulk water temperature about 2.2 °C over the course of the reaction.

Effect of Total Surface Area

Experiments were conducted to investigate the linearity of hydrogen generation as LiH pellet count – and surface area – was doubled and quadrupled. Figure 4 shows H₂ generation per pellet for experiments consisting of 1, 2, and 4 pellets at similar initial ambient temperature.

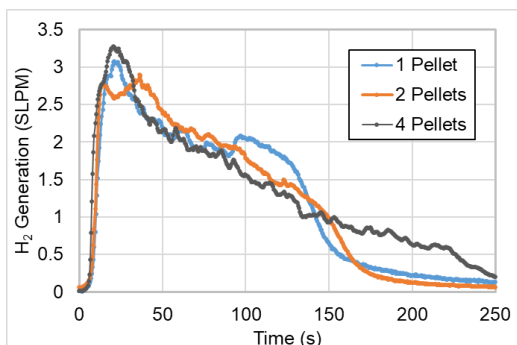


Figure 4. H₂ Generation per Pellet for Systems Containing 1, 2, and 4 Pellets at 221 kPa.

For this experimental system, the near overlay of data plots shows that the pellets react independently, despite the presence of other reacting pellets nearby. At least for systems consisting of 1–4 pellets, there appears to be sufficient and identical LiH–water contact such that H₂ generation is a linear function of total surface area.

Effect of Pressure

While most experiments with LiH were conducted at 221 kPa, a few were done at 386 kPa in order to investigate the effect of pressure, at least over a narrow range. Figure 5 overlays H₂ generation data from experiments at each pressure using 4 pellets.

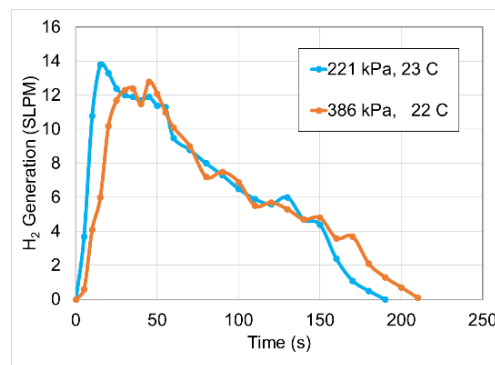


Figure 5. Comparison of H₂ Generation at 221 and 386 kPa for a 4 Pellet System.

The generation plots show little difference between the two pressures. The slight initial delay at 386 kPa is likely due to mechanical lag from the back pressure regulator.

Effect of Water Salinity – LiH and LiAlH₄

LiH experiments with 1 pellet were done in both fresh water and salt water (Instant Ocean mixed to simulate typical seawater). Figure 6 overlays data from each, which shows very similar generation curves.

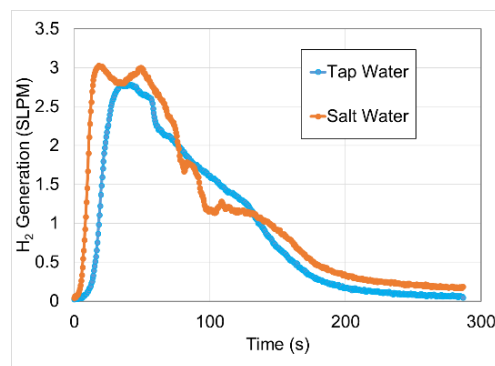


Figure 6. H₂ Generation from 1 LiH Pellet in Fresh and Salt Water at 221 kPa and 27 °C.

Thus, the salt ion concentration in seawater appears to have no effect on the LiH reaction mechanism.

However, the presence of dissolved salt for the LiAlH₄–water reaction appears to alter H₂ generation. Figure 7 compares LiAlH₄ experiments from both fresh and salt water. In the case of salt water, generation slows and fluctuates as compared to the bell-like curve from fresh water. Additional experiments with multiple LiAlH₄ pellets confirmed this result. It appears a solid, likely insoluble product forms near the reacting surface that impedes/blocks the normal transfer of water and/or release of H₂ from the

surface. This result plus product examination/identification will be investigated in future work.

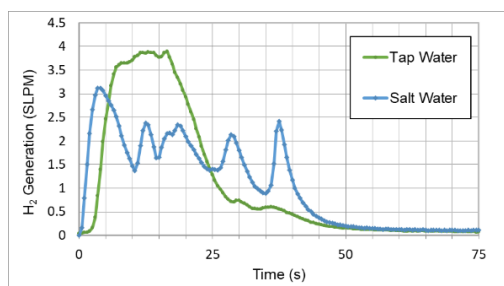


Figure 7. H₂ Generation from 1 LiAlH₄ Pellet in Fresh and Salt Water at 221 kPa and 25 °C.

Experiments with LiH Powder

Hydrogen generation data from the submerged reaction of monolayer LiH powder over a range of temperatures were used to derive required kinetic parameters k_0 and E_a for the mathematical model. The data, plotted in Figure 8, show the immediate generation of H₂ followed by a quick decay to zero within 5 seconds.

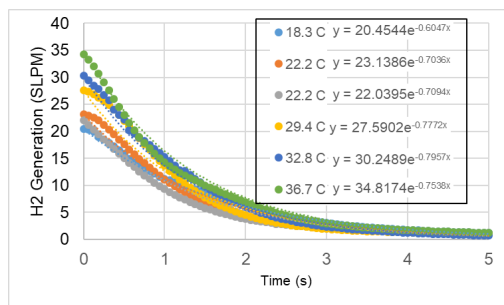


Figure 8. H₂ Generation from a Small Quantity of LiH Powder Over a Range of Temperatures.

Exponential fits of the data in combination with the Arrhenius equation led to derivation of $E_a = 8680$ J/mol and an average $k_0 = 0.133$ mm/s at $T = 293$ K. The derived E_a compares well to a previously reported value of 8360 J/mol [2].

Mathematical Model Development and Parameter Definitions

Data from the single pellet reactions were used along with the kinetic parameters found from powder reactions to fit the remaining parameters with the model. The governing equations were solved numerically within Mathematica and a nonlinear model fit was performed to minimize residuals created by manipulating V_w , h_0 , t_0 , and t_{eq} when compared with the experimental data. The dimensional model prediction is plotted alongside the data used for fitting in Figure 9.

The unknown parameters from equations 3 and 4 for the Figure 9 model fit were determined as follows:

- $E_a = 8680$ J/mol (Activation energy)

- $k_0 = 0.133$ mm/s (Initial surface reaction rate constant)
- $V_w = 29.4$ ml (Effective water volume)
- $h_0 = 141$ J/(s m² K) (Initial heat transfer coefficient)
- $t_0 = 17.6$ s (Heat transfer coefficient time parameter)
- $t_{eq} = 9.0$ s (Saturation concentration time parameter)

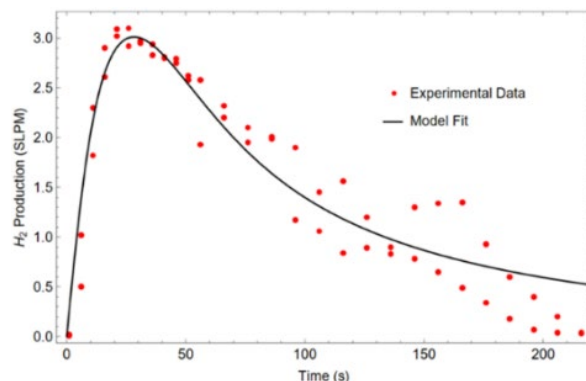


Figure 9. Model Fit for H₂ Generation for 1 LiH Pellet at 221 kPa and 20 °C Initial Temperature.

Discussion and Conclusions

This report presents only a portion of the collected experimental data and analysis accomplished to date. The authors intend to continue model development, including derivation of a dimensionless model that can be applied to a range of reactions and initial conditions.

Primary findings reported here include:

- LiH and LiAlH₄ are both H₂ dense solids that react very quickly and to completion when submerged in fresh water. The LiH reaction is unaffected in salt water, but the LiAlH₄ reaction is suppressed.
- Reaction rate increases with initial water temperature.
- H₂ generation is a linear function of surface area when there is sufficient water contact/flow to the surface.
- Reaction rate is not dependent on system pressure up to about 400 kPa.
- The reaction can be accurately modeled via mass and energy balance equations for time-varying, reacting systems, with identification of key model variables.

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2. Leckey, J.H., Nulf, L.E., and Kirkpatrick, J.R., "Reaction of Lithium Hydride with Water," *Langmuir*, 12 (26), 6361-6367, 1996.